Uniform semiclassical expansions for the direct part of Franck-Condon transitions

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Semiclassical expansions for traces involving Greens functions have two contributions, one from the periodic or recurrent orbits of the classical system and one from the phase space volume, i.e. the paths of infinitesimal length. Quantitative calculations require the control of both terms. Here, we discuss the contribution from paths of zero length with an emphasis on the application to Franck-Condon transitions. The expansion in the energy representation is asymptotic and a critical parameter is identified. In the time domain, a series expansion of the logarithm of the propagator gives very good results. The expansions are illustrated for transitions onto a linear potential and onto a harmonic oscillator.

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I. INTRODUCTION

Many quantum properties, including the density of states and Franck-Condon transition matrix elements can be expressed as a trace of the Greens function times some operator [1,2]. Semiclassical expressions for such quantities naturally divide up into two parts, one due to "paths of zero length" and one due to the longer recurrent or periodic trajectories of the associated classical system [3–6] The numerical and conceptual difficulties associated with the periodic orbit part have received considerable attention in the literature (see the contributions to [7,8] and the review [9]). Zeta functions have helped to overcome many of these problems, at least in certain, well-behaved situations [9–12]. More recently, higher order corrections to the dominant semiclassical contributions, in particular in the neighborhood of caustics and bifurcations have been addressed [12–18]. In applications to the photodissociation of molecules one has an additional source of corrections connected to the fact that the operator is a projection on the initial state and hence singular in the semiclassical limit. A way to deal with this has been proposed by Zobay and Alber [19].

In mainly direct reactions the largest part of the cross section comes, however, from the paths of zero length. This leading order term is also known as the Thomas-Fermi contribution for the case of smooth systems or the Weyl-term for billiards. It measures the volume of the energy shell in units of Planck's constant, raised to the power of the number of degrees of freedom present [3,4]. It turns out that in many situations one is too far away from this semiclassical limit (typically one needs a higher density of states) and so has to go beyond this leading order term. In billiards, the approximations to the density of states regularly contain the subdominant contributions from the surface and corner corrections, and even in smooth systems the leading order term alone will not do. The expansion in decreasing powers of energy or wave number, however, can typically be asymptotic at best. Building on their previous developments in the theory of asymptotic series, the behavior of the expansion has

been illustrated by Berry and Howls [20] for the case of billiards: the series expansion indeed diverges and the rate of divergence is determined by short real or imaginary orbits of the classical system.

In view of this it is perhaps not surprising that in semiclassical calculations of photodissociation cross sections one also has to go beyond the leading order terms and that one encounters the same kind of divergences [2,21,11]. For practical applications the problems then are how to estimate the importance of the higher order terms (without calculating them, of course) and how to improve on the series expansion. We will show here that comparison to a simpler problem, namely excitation onto a linear potential, suggests a useful parameter. For the second problem we analyze in some detail the behavior of three different approximations to the background term and identify the most useful one. For the sake of simplicity in notation all our calculations will be confined to one degree of freedom only. Generalizations to more degrees of freedom are straightforward. The main ideas will be illustrated for transitions onto a linear potential and onto a harmonic potential. Applications to photodissociation of water will be given elsewhere [39].

Various theoretical aspects of the classical and semiclassical limit of Franck-Condon transitions have been discussed previously in the literature. Much of the history is reviewed in the paper by Dowling et al. [22], where also an interesting alternative phase space interpretation for Franck-Condon transitions can be found. Applications to molecules can be found in the books [23,24]. Of particular relevance for our discussion is a paper by Heller [2] which contains background information as well as a discussion of the first few correction terms; we summarize some of his results in section IIA. Approximations in the time domain (which we take up in section 3) have been discussed e.g. in [25–27].

The outline of the paper is as follows. In section 2 we discuss the Wigner- and the Grammaticos and Voros-expansion in the energy representation. The behavior at large orders for a linear potential is analyzed in section 3. In section 4 we study approximations in the time domain,

which can then be connected to the energy domain by a Fourier transform (perhaps to be evaluated numerically). The quality of the approximations is illustrated for the harmonic oscillator in section 5. Some conclusions will be drawn in section 5.

II. SEMICLASSICAL FRANCK-CONDON FACTORS

A. The Wigner series

We consider transitions from an initial state Ψ_i, typically a Gaussian, to a manifold of final states Ψ_E at energy E. The system has one degree of freedom and the classical Hamiltonian on the upper potential energy surface is given by

$$H(p, q) = \frac{p^2}{2m} + V(q). \qquad (1)$$

Quantum operators will be denoted with a '^', so that e.g. the quantum Hamilton operator will be $\hat{H}$. The Frank-Condon factors we want to calculate are the squares of the transition elements [2,23,24],

$$\rho(E) = |\langle \Psi_i | \Psi_E \rangle|^2. \qquad (2)$$

Using $|\Psi_E\rangle\langle\Psi_E| = \delta(E - \hat{H})$, where $\hat{H}$ is the Hamilton operator for the final electronic state, we can write the Franck-Condon factor as

$$\rho(E) = \langle \Psi_i | \delta(E - \hat{H}) | \Psi_i \rangle \qquad (3)$$

$$= \int_{-\infty}^{+\infty} dx \, \langle \Psi_i | x \rangle \langle x | \delta(E - \hat{H}) | \Psi_i \rangle \qquad (4)$$

$$= \operatorname{tr} \delta(E - \hat{H})\hat{\Pi}, \qquad (5)$$

which has the above mentioned form as a trace over a Greens function,

$$\delta(E - \hat{H}) = -\frac{1}{\pi} \operatorname{Im} \lim_{\varepsilon \to 0} \hat{G}(E + i\varepsilon) \qquad (6)$$

$$= \frac{1}{\pi} \operatorname{Im} \lim_{\varepsilon \to 0} \frac{1}{E - \hat{H} + i\varepsilon}, \qquad \varepsilon > 0 \qquad (7)$$

times the projector $\hat{\Pi} = |\Psi_i\rangle\langle\Psi_i|$ onto the initial state. Taking the Wigner transform of this expression one arrives at classical phase space traces over the Wigner transforms of the operators involved [28],

$$\rho(E) = \frac{1}{h} \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dq \, [\delta(E - \hat{H})]_W(p, q) \, [\hat{\Pi}]_W(p, q). \qquad (8)$$

where the Wigner transform of an operator $\hat{A}$ is given by [28,29]:

$$[\hat{A}]_W(p, q) = \int dx \, e^{-ixp/\hbar} \left\langle q + \frac{x}{2} \middle| \hat{A} \middle| q - \frac{x}{2} \right\rangle. \qquad (9)$$

It is interesting to note that under the trace the Wigner transform of the product of two operators maps into the product of the Wigner transforms. Generally, for a product of operators one has

$$[\hat{A}\hat{B}]_W(p, q) = [\hat{A}]_W(p, q) \exp\left\{\frac{i\hbar}{2}\Lambda\right\} [\hat{B}]_W(p, q) \qquad (10)$$

with the differential operator

$$\Lambda = \overleftarrow{\nabla}_p \quad \overrightarrow{\nabla}_q \quad - \quad \overleftarrow{\nabla}_q \quad \overrightarrow{\nabla}_p \qquad (11)$$

where the differentiations act to the left or to the right as indicated. If the Hamilton operator is simply replaced by the classical Hamilton function, the leading order term for the density of states, the microcanonical measure on the energy shell, $[\delta(E - \hat{H})]_W \sim \delta(E - H)$, is obtained. The fact that formation of products and Wigner transforms does not commute is the source of quantum corrections which we want to study.

A systematic procedure to calculating an expansion of the density of states in powers of $\hbar$ was suggested long ago by Wigner [29] and applied to the Franck-Condon problem by Heller [2]. It uses the statistical operator $\hat{P} = \exp(-\beta\hat{H})$ and its high temperature expansion for $\beta \to 0$. The statistical operator satisfies

$$-\frac{\partial}{\partial\beta}\hat{P} = \hat{H}\hat{P} = \frac{1}{2}\left(\hat{H}\hat{P} + \hat{P}\hat{H}\right). \qquad (12)$$

The symmetrized version on the right hand side is particularly well suited for application of the Wigner transformation as it immediately shows that the quantum corrections come in even powers of $\hbar$ only. Using (10) for the product of two operators the equation for $[\hat{P}]_W$ becomes

$$-\frac{\partial}{\partial\beta}[\hat{P}]_W = [\hat{H}]_W \cos\left\{\frac{\hbar}{2}\Lambda\right\} [\hat{P}]_W. \qquad (13)$$

The first few terms can be calculated by substitution of the ansatz

$$[\hat{P}]_W = e^{-\beta H} \left(1 + \hbar^2 c_2 + \hbar^4 c_4 + \dots\right). \qquad (14)$$

This expansion contains only even powers of $\hbar$ because of the symmetrization in (12). Each coefficient c_n is itself a polynomial in β. For later reference we quote c_2 for the Hamiltonian (1) [2,29],

$$c_2 = -\beta^2 f_2 + \beta^3 f_3 \qquad (15)$$

with

$$f_2 = \frac{1}{8m}V'' \qquad (16)$$

$$f_3 = \frac{1}{24m}V'^2 + \frac{1}{24m^2}V''p^2 \qquad (17)$$

where the primes denote derivatives with respect to position.

The statistical operator is the Laplace transform of the density of states, so to get back the quantity needed in the phase space trace, we need to do an inverse Laplace transform (see [2] for more details). The leading exponential then maps into the delta function on the classical energy shell, $\delta(E - H)$, and the powers of β map into derivatives of the delta function with respect to energy. The resulting expansion thus becomes

$$
[\delta(E - \hat{H})]_W = \delta(E - H)
$$
$$
-\hbar^2 f_2 \frac{\partial^2}{\partial E^2} \delta(E - H) + \hbar^2 f_3 \frac{\partial^3}{\partial E^3} \delta(E - H)
$$
$$
+\hbar^4 \dots . \tag{18}
$$

Heller [2] noted that instead of expanding in the form of an exponential times a power series in β, one could alternatively expand as the exponential of a power series. For the terms given above this leads to an Airy function approximation,

$$
[\delta(E - \hat{H})]_W = \exp\left\{-(H - E)f_2/3f_3 - 2\hbar^2 f_2^3/27f_3^2\right\}
$$
$$
\cdot \alpha \operatorname{Ai}(\alpha(H - E + \hbar^2 f_2^2/f_3)) \tag{19}
$$

with

$$
\alpha = (3\hbar^2 f_3)^{-1/3} . \tag{20}
$$

Up to and including terms of order $\hbar^2$ the delta-function expansion of the Airy function in (19) is equivalent to the Wigner expansion (18). We will come back to this Airy function approximation below.

B. The Grammaticos and Voros expansion

The Wigner method of the previous section is a bit tedious when it comes to calculating higher oder terms. A very convenient algebraic method of expansion was developed by Grammaticos and Voros [30]. The Dirac measure $[\delta(E - \hat{H})]_W$ is expanded around the identity operator $\hat{I}$ times the classical Hamilton function, $H(p,q) \cdot \hat{I}$. The resulting series contains powers of the deviations $\hat{H} - H\hat{I}$, which have an explicit $\hbar$ dependence because of the Wigner equivalent of the product of two operators, Eq. 10. To obtain this expansion, start from the integral representation,

$$
\delta(E - \hat{H})
$$
$$
= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{iEt/\hbar} e^{-i\hat{H}t/\hbar} dt \tag{21}
$$
$$
= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i(E-H)t/\hbar} e^{-i(\hat{H}-H\hat{I}))t/\hbar} dt \tag{22}
$$
$$
= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i(E-H)t/\hbar} \sum_{r=0}^{\infty} \frac{(-it)^r}{r!\hbar^r} (\hat{H} - H\hat{I})^r dt . \tag{23}
$$

Next, take the Wigner transform on both sides and interchange summation and integration,

$$
[\delta(E - \hat{H})]_W
$$
$$
= \frac{1}{2\pi\hbar} \sum_{r=0}^{\infty} \frac{(-1)^r}{r!} \int_{-\infty}^{\infty} dt \left(\frac{it}{\hbar}\right)^r e^{i(E-H)t/\hbar} \left[(\hat{H} - H\hat{I})^r\right]_W \tag{24}
$$
$$
= \sum_{r=0}^{\infty} \frac{(-1)^r}{r!} \delta^{(r)}(E - H(p,q)) \mathcal{G}_r(p,q,\hbar) . \tag{25}
$$

The derivatives of the delta function are with respect to the energy (as in (18)) and the universal coefficients $\mathcal{G}_r$ are the Wigner transforms of powers of the Hamiltonian,

$$
\mathcal{G}_r(p,q,\hbar) = \left[(\hat{H} - H(p,q)\hat{I})^r\right]_W . \tag{26}
$$

They are universal in that other functions of the Hamiltonian can be obtained by integration over energy, e.g.

$$
[f(\hat{H})]_W = \int_{-\infty}^{+\infty} dE \, f(E) \, \delta(E - \hat{H}) \tag{27}
$$
$$
= \sum_{r=0}^{\infty} \frac{1}{r!} f^{(r)}(H(p,q)) \mathcal{G}_r(p,q,\hbar) , \tag{28}
$$

and will contain the same coefficients. We will use this transformation for the statistical operator and the Greens function below.

In principle, the $\mathcal{G}_r$ could be calculated by straightforward expansions of the powers, and subsequent Wigner-transformation. However, Grammaticos and Voros [30] give a more efficient algebraic technique, using Greens functions. They consider the transformation (28) with $f(\hat{H}) = 1/(\hat{H} - z)$ and thus find for Greens function

$$
[\hat{G}]_W(p,q,\hbar) = \sum_{r=0}^{\infty} (-1)^r \frac{\mathcal{G}_r(p,q,\hbar)}{(H(p,q) - z)^{r+1}} . \tag{29}
$$

The $\mathcal{G}_r$ can be read off from an expansion of $[\hat{G}]_W(p,q,\hbar)$ in inverse powers of $(H - z)^{-r-1}$. The Greens function satisfies $(\hat{H} - z)\hat{G}(z) = \hat{I}$. Using the symmetrized version as in (12) and (13), this becomes in the Wigner representation

$$
[\hat{I}]_W = 1 = [(\hat{H} - z)\hat{G}(z)]_W \tag{30}
$$
$$
= [(\hat{H} - z)]_W \cos\left(\frac{\hbar}{2}\Lambda\right) [\hat{G}]_W(z)
$$
$$
= (H - z)[\hat{G}]_W + \sum_{n=1}^{\infty} \hbar^{2n} \mathcal{H}_{2n}[\hat{G}]_W . \tag{31}
$$

The expansion in powers of $\hbar$ in the last line defines differential operators $\mathcal{H}_n(p,q,\nabla_p,\nabla_q)$. For $n = 2, 4$ and the Hamiltonian (1) they are

$$
\mathcal{H}_2 = -\frac{1}{8}\left(\frac{1}{m}\frac{\partial^2}{\partial q^2} + \frac{\partial^2 V(q)}{\partial q^2}\frac{\partial^2}{\partial p^2}\right) , \tag{32}
$$
$$
\mathcal{H}_4 = \frac{1}{384}\frac{\partial^4 V(q)}{\partial q^4}\frac{\partial^4}{\partial p^4} . \tag{33}
$$

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The Wigner transform of Greens function can be expanded in powers of $\hbar$ as well,

$$[\hat{G}]_W(p,q,z,\hbar) = \sum_{m=0}^{\infty} \hbar^m G_m(p,q,z) \, , \qquad (34)$$

and comparison of like powers of $\hbar$ in (30) then gives recursion relations for the coefficients G_m,

$$G_0(p,q,z) = \frac{1}{H-z} \, , \qquad (35)$$

$$G_{2n}(p,q,z) = -\frac{1}{H-z}\left(\sum_{k=1}^{n} \mathcal{H}_{2k} G_{2(n-k)}\right) \, . \qquad (36)$$

Odd powers in $\hbar$ vanish because of symmetrization (as in (12,13)).

Putting everything together one notes that by this method the Greens function becomes a double series, organized in powers of $\hbar$ and in inverse powers of $(H-z)$. Expression (34) emphasizes the former and (29) the latter, so that the $\mathcal{G}_r$ can be obtained from (36) by collecting contributions with the same powers of $(H-z)^{-r-1}$. The structure of the expansion is such that there are always finitely many contributions to the coefficients $\mathcal{G}_r$ (for an example see the expansion for the harmonic oscillator in (94) below). The first few coefficients are

$$\mathcal{G}_0 = 1 \, , \qquad (37)$$

$$\mathcal{G}_1 = 0 \, , \qquad (38)$$

$$\mathcal{G}_2 = -\frac{\hbar^2}{4m}\frac{\partial^2 V(q)}{\partial q^2} \, , \qquad (39)$$

$$\mathcal{G}_3 = -\frac{\hbar^2}{4m}\left(\frac{\partial V(q)}{\partial q}\right)^2 - \frac{\hbar^2 p^2}{4m^2}\frac{\partial^2 V(q)}{\partial q^2} + \frac{3\hbar^4}{64m^2}\frac{\partial^4 V(q)}{\partial q^4} \, . \qquad (40)$$

Given these expansions, we now investigate their large order behavior, first for the linear potential already studied by Heller [2].

III. LINEAR REPULSIVE POTENTIAL

A. The quantum case

The simplest model for a Franck-Condon transition onto a dissociating potential describes transitions from a Gaussian initial state

$$\langle x|\Psi_i\rangle = \frac{1}{\pi^{1/4}\sigma^{1/2}}e^{-(x-x_0)^2/2\sigma^2} \, , \qquad (41)$$

onto a linear potential with Hamilton operator

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta - ax \, . \qquad (42)$$

This model can be solved analytically and can be used as an approximation for transitions in an arbitrary potential if a is taken to be the slope of the upper potential energy surface at the maximum of the Gaussian initial state (which here is centered at $q_0 = 0$). Lengths $\tilde{q} = q/\lambda$ can conveniently be measured in units of

$$\lambda = (\hbar^2/2ma)^{1/3} \qquad (43)$$

and energy in units of $a\lambda$, i.e $\epsilon = E/a\lambda$. The eigenfunctions for this potential are Airy functions, and λ sets the scale for the width of the oscillations near the turning point; the other oscillations in the wave function have shorter wave length. The Franck-Condon matrix elements can also be calculated exactly,

$$\rho(\varepsilon) = \frac{1}{a\sqrt{\pi}\sigma}\left|\int_{-\infty}^{\infty} e^{-\tilde{q}^2 s^2/2}\mathrm{Ai}(-(\tilde{q}+\varepsilon))d\tilde{q}\right|^2 \, , \qquad (44)$$

$$= \frac{2\sigma\sqrt{\pi}}{a\lambda^2}\mathrm{Ai}^2\left(\frac{1}{4}s^{-4} - \varepsilon\right)e^{s^{-6}/6 - \varepsilon s^{-2}} \, . \qquad (45)$$

They depend on energy and on the ratio

$$s = \lambda/\sigma \qquad (46)$$

of the length scale of the continuum wavefunction to the width of the initial state. This parameter also contains $\hbar$ and thus indicates how 'semiclassical' one is. For small s, i.e. small $\hbar$ or large σ and a broad initial state, the transition integral will average over many of the oscillations of the Airy function and one can expect the leading classical term to be reasonably accurate. However, for large s and narrow Gaussians, the initial state will probe every fine detail of the Airy function and the classical approximation will presumably not work well. We will come back to this point in section IV B. It is our aim now to show how these quantum expectations are reflected in the semiclassical expansion. As a first step we need to calculate the terms in the series (25).

B. Asymptotic expansions for a linear potential

For the Hamiltonian (42) with its linear potential, equation (31) contains only a single differential operator,

$$\mathcal{H}_2 = -\frac{1}{8}(H-z)\Lambda^2$$

$$= -\frac{1}{8m}\frac{\partial^2}{\partial q^2} \, ,$$

all higher operators vanish. Then the recursion relations for the G_{2n} reduce to

$$G_{2n} = -G_0\mathcal{H}_2 G_{2(n-1)} \, . \qquad (47)$$

Since

4

$$G_0 = \frac{1}{H - z} = \frac{1}{\frac{p^2}{2m} - aq - z} \qquad (48)$$

is linear in q, the action of $\mathcal{H}_2$ on powers of G_0 is

$$\mathcal{H}_2 G_0^n = -\frac{1}{8m} a^2 n(n+1) G_0^{n+2} . \qquad (49)$$

Together with the pre-factor $-G_0$ the coefficients G_{2n} become

$$G_{2n} = \left(\frac{a^2}{8m}\right)^n \frac{(3n)!}{3^n n!} G_0^{3n+1} . \qquad (50)$$

Comparing the expansion

$$[\hat{G}]_W = \sum_{n=0}^{\infty} \left(\frac{a^2}{8m}\right)^n \hbar^{2n} \frac{(3n)!}{3^n n!} \frac{1}{(H - z)^{3n+1}} \qquad (51)$$

to the $\hbar$ - expansion of $[\hat{G}]_W$ in Eq. (29) one can easily read off the coefficients $\mathcal{G}_r$. The asymptotic series (25) for the Dirac phase space measure then becomes

$$[\delta(E - \hat{H})]_W = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{a^2 \hbar^2}{24m}\right)^n \delta^{(3n)}(E - H(x,p)) . \qquad (52)$$

This may be compared to the exact form of $[\delta(E - \hat{H})]_W$ computed from the exact propagator,

$$[\delta(E - \hat{H})]_W$$
$$= \mathrm{Ai}\left(\frac{E - \frac{1}{2m}p^2 + aq}{\left(\frac{a^2 \hbar^2}{8m}\right)^{1/3}}\right) \frac{1}{\left(\frac{a^2 \hbar^2}{8m}\right)^{1/3}}$$
$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dz \ \exp\left\{i(E - H)z - i\frac{a^2 \hbar^2}{24m} z^3\right\} , \qquad (53)$$

where z is a dimensionless integration variable. The sequence of delta functions and their derivatives may be obtained [2] by expanding the exponential with the z^3 term in a power series and interchanging integration and summation,

$$[\delta(E - \hat{H})]_W$$
$$= \frac{1}{2\pi} \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{a^2 \hbar^2}{24m}\right)^n \int_{-\infty}^{\infty} dz (-iz^3)^n e^{i(E-H)z}$$
$$= \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{a^2 \hbar^2}{24m}\right)^n \delta^{(3n)}(E - H) . \qquad (54)$$

These formulae can now be used for the calculation of the Franck-Condon factors.

C. Asymptotic behavior

The Wigner transform of the initial Gaussian is a Gaussian in phase space,

$$\Pi_W(q, p) = 2 \exp\left\{-\frac{(q - q_0)^2}{\sigma^2} - \frac{\sigma^2 p^2}{\hbar^2}\right\} , \qquad (55)$$

which helps to limit the domain of integration in (8) especially in cases of dissociation processes where the classical phase space is unbounded in certain directions. The expansion for the density of states, eq. (54), then gives for the series expansion of the Franck-Condon factor

$$\rho_{\mathrm{asymp}}(\varepsilon) = \frac{2}{\pi a \lambda} \sum_{n=0}^{\infty} \frac{s^{3n}}{12^n n!} I_n(\varepsilon, s) \qquad (56)$$

with the integrals

$$I_n(\varepsilon, s) = \int_0^{\infty} e^{-(x^2 - \varepsilon)^2 s^2 - x^2/s^2} H_{3n}((x^2 - \varepsilon)s) dx . \qquad (57)$$

Just as the exact quantum result the expansion contains only a single parameter, $s = \lambda/\sigma$. The behavior for different values of s at $\varepsilon = 0$, i.e. for the maximum of the packet, is indicated in Fig. 1. For small s the terms decay rapidly and up to high n, but eventually they start to grow and to diverge rapidly: this is the behavior expected for an asymptotic series. As s increases, the turnover to divergence comes for smaller n and for s near 1 all higher order terms are larger than the first one. In Table I we list the index of the smallest term as well as its size for several values of s.

To estimate the rate of divergence of the series, one can substitute the generating function for the Hermite polynomials and express the integrals (57) for $\varepsilon = 0$ as

$$I_n(s) = \frac{\partial^{3n}}{\partial t^{3n}} \left(\int_0^{\infty} dx e^{-(x^2 - \varepsilon)^2 s^2 - x^2/s^2 + 2t(x^2 \varepsilon)s - t^2}\right)\bigg|_{t=0} . \qquad (58)$$

This integral cannot be solved exactly. In saddle point approximation for small s one finds just a single saddle (for some ε there are three). The results is

$$I_n(s) = \frac{\partial^{3n}}{\partial t^{3n}} \left(\frac{\sqrt{\pi}}{2} \frac{s}{\sqrt{1 - 2ts^3}} e^{-t^2}\right)\bigg|_{t=0} . \qquad (59)$$

Expanding in powers of t, one finally arrives at

$$I_n(s) = \frac{\sqrt{\pi}}{2} (3n)! \sum_{2l+r=3n} \frac{(-1)^l}{l!} (2s^3)^{r+1} \binom{-1/2}{r} , \qquad (60)$$

clearly showing a leading order behavior for small s of the form

$$I_n(s) \approx \begin{cases} (-1)^{3n/2} \frac{\sqrt{\pi}}{2} \frac{(3n)!}{(3n/2)!} s & n \text{ even,} \\[2ex] (-1)^{(3n+1)/2} \frac{\sqrt{\pi}}{2} \frac{(3n)!}{((3n-1)/2)!} s^4 & n \text{ odd.} \end{cases} \qquad (61)$$

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Together with the other prefactors in (56) a typical term in the sum for n even is

$$\frac{(-1)^{3n/2}}{\sqrt{\pi}a\lambda}\frac{(3n)!}{12^n\,n!(3n/2)!}s^{3n+1},\qquad(62)$$

and similarly for n odd. With the help of Stirlings formula, one can estimate the size of this term to be of the order $[\sqrt{6}(n/12\,\mathrm{e})^{1/3}s]^{3n}$. The terms start to grow once the square bracket becomes larger than one, i.e. for $n > n_c \approx (2\mathrm{e}/\sqrt{6})\,s^{-3}$. This strong s dependence is in accord with the variations in Fig. 1.

The information gained from this analysis of the linear potential can be used in more general settings: for excitations into some arbitrary potential $V(q)$, the parameter a can be estimated from the slope of the potential at the maximum q_0 of the initial state, $a = -V'(q_0)$. If the parameter s thus formed is small, the classical approximation will be good (and the corrections small), whereas some uniform approximation has to be tried if s is large.

IV. TIME-DOMAIN APPROXIMATIONS

A. The formal theory

Another approach to the calculation of the mean density of states exploits the relationship between energy- and time-domain. Since the mean parts are obtained by averaging over (large) energy intervals, they correspond to short time properties. This is the way the background is obtained in numerical calculations: the wave packet is propagated for a time long enough so that the overlap with the initial wave packet is minimal but short enough so that no major part has returned, yet. This finite time window is then Fourier transformed to obtain the background term.

This can be mimicked in the semiclassical approximation. The Franck-Condon factors are related to Feynman's propagator in phase space by

$$\rho(E) = \frac{1}{\pi\hbar}\mathrm{Re}\int_0^\infty dt \int \frac{dqdp}{h}e^{iEt/\hbar}[\hat{\Pi}]_W(p,q)\,[\hat{K}]_W(p,q),\qquad(63)$$

where $[\hat{K}]_W$ is the Wigner transform of the propagator

$$[\hat{K}]_W(p,q) = \int dx\,e^{-ixp/\hbar}\left\langle q+\frac{x}{2}\middle| e^{-i\hat{H}t/\hbar}\middle| q-\frac{x}{2}\right\rangle.\qquad(64)$$

In the standard semiclassical approximation the smooth part of the Franck-Condon factor is obtained by use of the short time propagator from $q - x/2$ to $q + x/2$ for Eq. (64). In the simplest approximation (e.g. Berry and Mount 1972), $\hat{K}$ is replaced by a propagator for a free particle in a constant potential $V(q)$,

$$K(q+x/2,q-x/2,t) = \left(\frac{m}{2\pi i\hbar t}\right)^{1/2}e^{i\left(\frac{m}{2t}x^2-V(q)t\right)/\hbar}.\qquad(65)$$

The dominant part of the Franck-Condon factor as a function of the energy will come from that region in energy where the turning point of the classical motion on the upper surface is near to the maximum of the initial state. The ultimate form of this is the reflection principle, where the wave function on the upper surface is replaced by a delta function so that the cross section is obtained by 'reflection' of the initial state on the potential energy surface (see [2,23] for a discussion of its origin and its limitations). This implies that the straight line propagator on a constant potential is a rather poor approximation since it does not account for a turning point nor the exponential damping when entering the forbidden region (See Fig. 2).

To obtain a better approximation linearize the potential around the center point q of the propagator,

$$V(q') = V(q + (q' - q)) \approx V(q) + V'(q)\,(q' - q),\quad(66)$$

and use the exact propagator for the Lagrangian

$$\mathcal{L}(\dot{q}',q') = \sum_i \frac{m_i}{2}\dot{q}'^2 - V'(q)\,q' - V(q) + V'(q)\,q,\quad(67)$$

viz.,

$$K(q+x/2,q-x/2,t) =$$
$$\left(\frac{m}{2\pi i\hbar t}\right)^{1/2}\exp\left(\frac{i}{\hbar}\left[\frac{m}{2t}x^2 - V(q) - \frac{V'(q)^2}{24m}t^3\right]\right).\qquad(68)$$

The integration over x and time gives an Airy function phase space density,

$$\sigma_0(E) = \int \frac{dpdp}{h^N}\,\tilde{\alpha}\,\mathrm{Ai}\,(\tilde{\alpha}\,(H(q,p) - E))\,[\hat{\Pi}]_W(q,p)\quad(69)$$

with

$$\tilde{\alpha} = \left(\frac{\hbar^2|V'(q)|^2}{8m}\right)^{-1/3}.\qquad(70)$$

Comparison with the Airy function approximation introduced by Heller, (19) and (20), shows that the two coincide for a linear potential: then $V'' = 0$ as well as $f_2 = 0$ and the two scales (20) and (70) agree.

The above approximative formula for the direct part of Franck-Condon factors is exact for a linear potential and contains an interesting limit case, the one of an almost flat potential.

6

B. Recurrence resonances

If the potential vanishes, $a = 0$ in (42), the Gaussian simply spreads and the Franck-Condon factor becomes

$$\rho_{\text{free}}(E) = \sqrt{\frac{2m\sigma^2}{\pi\hbar^2}} \frac{e^{-2mE\sigma^2/\hbar^2}}{\sqrt{E}} . \tag{71}$$

When $a = 0$ is substituted in (69), the scale $\tilde{\alpha}$ becomes infinite and the limit is singular. Similarly, the parameter s goes to infinity, indicating that the transition proceeds via the full quantum regime. Note that in the series expansion (52) the transition can be performed easily, the coefficients of the derivatives of the delta function vanish. This shows that the effect to be discussed here is non-perturbative.

On the classical side, the limit is also singular in a certain sense. Fix the energy and consider the classical trajectories starting at some point q_0. For vanishing potential, there are two straight line trajectories running off to positive or negative infinity, depending on momenta. As soon as there is a sloping potential, no matter how small a, the topology changes (see Fig. 3). For negative a, the trajectories running off to plus infinity will pick up in speed but be otherwise unchanged. The ones going towards negative infinity, however, run up to the potential and will have to return after some time. The position of this turning point, $q_c = -E/a$ if E is the kinetic energy at q_0, moves further out the smaller a and also the time for the trajectory to return increases with decreasing a. The consequences of this are that the return of the classical trajectory introduces a long time scale, which, upon Fourier transform to the energy domain, will manifest itself in a modulation on small energy differences.

These modulations are observed in the exact Franck-Condon factor (45) in the case of large parameter s, as then the structure from the Ai²-part dominates (See Fig. 4). A WBK quantization allows to connect the oscillations with recurrent orbits.

The positions of the 'resonances' in the exact Franck-Condon factor eq.(45) are given by the zeros of the first derivative of the Airy function which are approximately described by [31]:

$$\varepsilon_n = \left(\frac{3\pi}{2} \left(n + \frac{1}{4} \right) \right)^{2/3} \frac{1}{4} s^{-4} \tag{72}$$

If we quantize semiclassically the action of the closed (recurrent) orbit which starts in the center of the Gaussian, is reflected by the potential and returns to the initial point with reversed momentum by requiring that

$$S(E) = \frac{2}{\hbar} \int_0^{-\varepsilon\lambda} \sqrt{2m(E+ax)} dx = 2\pi(n + \tfrac{1}{4}) \tag{73}$$

(note that there is just one turning point, hence the contribution $1/4$ instead of $1/2$ from the Maslov indices) we obtain resonance positions

$$\varepsilon_n^{sc} = \left(\frac{3\pi}{2} \left(n + \frac{1}{4} \right) \right)^{2/3} . \tag{74}$$

The quantization assumes orbits starting and ending in the center of the Gaussian and hence becomes more accurate for a narrow Gaussian.

In the limit $s \to 0$ these oscillations are suppressed: The initial Gaussian has a momentum distribution $e^{-\tilde{p}^2 s^{-2}}$ which is more concentrated around zero for small s. If we regard the initial wavepacket as a cloud of particles with this momentum distribution, it will move quite uniformly for small s, whereas for large s the cloud will spread quickly. The fast moving parts are reflected and interfere with the slowly moving parts. As the particles obey $\varepsilon = \tilde{p}^2 - \tilde{q}$, their energy distribution in the center of the Gaussian, $\tilde{q} = 0$, is $e^{-\varepsilon s^{-2}}$. This energy distribution factor is responsible for the damping of the oscillations in the full cross section eq.(45).

If we take a look at the exact autocorrelation function,

$$C(t) = \frac{1}{\sqrt{1 + its^2}} e^{-t^2/4s^2 - it^3/12} , \tag{75}$$

we have in the limit of the reflection principle

$$C(t) \xrightarrow{s \to 0} e^{-t^2/4s^2} , \tag{76}$$

which results in a Gaussian cross section. In the other limit

$$C(t) \xrightarrow{s \to \infty} \frac{1}{\sqrt{1 + its^2}} e^{-it^3/12} , \tag{77}$$

the first part resembles the autocorrelation function of a freely moving spreading wavepacket, but the second oscillating term accounts for the recurrent path contributions to the propagator.

It is therefore reasonable to term the oscillating structures 'recurrence resonances'. Although they are not connected to periodic orbits which imply infinitely many revivals they are associated with recurrent orbits, and their autocorrelation function differs from that of a simply spreading wavepacket.

Already Condon [32] and then later Hunt and Child [33] and Tellinghuisen [34] have mentioned these oscillations to appear on very shallow dissociative potentials and described them with the help of an opposite reflection principle, namely that the continuum wave function is reflected in the cross section [33]: For large s, we have in the Franck-Condon factor eq.(44): the initial state centered at $\tilde{q} = 0$ which acts like a needle scanning the continuum state:

$$\frac{e^{-\tilde{q}^2 s^2/2}}{\sqrt{2\pi}\sigma} \xrightarrow{s \to \infty} \delta(\tilde{q}) \tag{78}$$

and the cross section becomes

$$\rho(\varepsilon) = \frac{2\sigma\sqrt{\pi}}{V'\lambda^2} \text{Ai}^2(-\varepsilon) \tag{79}$$

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This example nicely illustrates the importance of recurrent orbits since they are responsible for ALL the structures which often would be associated with periodic orbits.

C. Higher order approximations in the time domain

In both the energy and the time domain, the Airy functions are intuitively appealing approximations based on the first few correction terms, but it is not obvious how to systematically improve on them. A most convenient method uses the Wigner expansion of the time propagator, obtained from (28) with the Grammaticos and Voros method and the universal coefficients $\mathcal{G}_r$, compare eq. (25). The Wigner transform of the propagator has the expansion

$$\left[e^{-i\hat{H}t/\hbar}\right]_W = \sum_{r=0}^{\infty} \frac{(-it)^r}{r!\hbar^r} e^{-iHt/\hbar}\mathcal{G}_r(q,p,\hbar)\,, \qquad (80)$$

with the same $\mathcal{G}_r$ as calculated before. This means that the autocorrelation function of the wave function,

$$C(t) = \langle\Psi_i|\Psi_r\rangle = \mathrm{tr}\, e^{-i\hat{H}t/\hbar}\hat{\Pi} \qquad (81)$$

$$= \frac{1}{h}\int dp\,dq\, \left[e^{-i\hat{H}t/\hbar}\right]_W (p,q)\,[\hat{\Pi}]_W(p,q) \qquad (82)$$

can be constructed with the help of this series. The p-integrations can always be done analytically and we are left only with the coordinate integrations. The cross section is then obtained by a Fourier transform,

$$\rho(E) = \frac{2}{h}\mathrm{Re}\int_0^{\infty} e^{iEt/\hbar}C(t)\chi(t)\,, \qquad (83)$$

where $\chi(t)$ is a window function that confines the region of integration to the short times needed for the direct part. This window is moreover important as the terms in the expansion (80) may grow without bound for large time, influencing the convergence of the integrals. As soon as terms beyond the linear potential approximation are included the autocorrelation function may show recurrences structures which have to be switched off by means of a window.

Eq. 82 has the advantage over (18) that it avoids the energy derivatives which impose the highest demands on the numerical accuracy of the phase space integrations. The Fourier transform to energy can be done effectively using fast Fourier transforms. However, if the series expansion (80) is used directly, the high powers for large times have a devastating effect numerically and nothing is gained. A way out of this dilemma is suggested by the manipulations that lead to (54). Perhaps it is possible to sum the power series expression in t in (80) into some exponentiated form, the first term of which would be an Airy function. This may be achieved using

$$\sum_r \frac{(-it)^r}{r!\hbar^r}\mathcal{G}_r = \exp\left\{-i\sum_k \mathcal{F}_k t^k \hbar^{-k}\right\}\,. \qquad (84)$$

The expansion coefficients $\mathcal{G}_r$ are known from the algebra in the energy representation and the coefficients $\mathcal{F}_k$ can be obtained from the Plemelj-Smithies recursion relations [35–37]

$$\mathcal{F}_n = \frac{(-1)^n i^{n+1}}{n!}\mathcal{G}_n - \frac{1}{n}\sum_{k=1}^{n-1} k\mathcal{F}_k \frac{(-1)^{n-k} i^{n-k}}{(n-k)!}\mathcal{G}_{n-k}\,. \qquad (85)$$

Since for $t = 0$ we must have $\left[e^{-i(\hat{H}-H)t/\hbar}\right]_W = 1$, the coefficient $\mathcal{F}_0 = 0$. The next few are

$$\mathcal{F}_1 = 0\,, \qquad (86)$$

$$\mathcal{F}_2 = -\frac{i}{2}\mathcal{G}_2\,, \qquad (87)$$

$$\mathcal{F}_3 = -\frac{1}{6}\mathcal{G}_3\,, \qquad (88)$$

$$\mathcal{F}_4 = \frac{i}{4}\left(\frac{1}{6}\mathcal{G}_4 - \mathcal{G}_2^2\right)\,. \qquad (89)$$

The above formulas have an interesting phase space interpretation: According to Berry [38] we have now taken into account the fringes in phase space surrounding the energy shell. The difference to Berry's fringes-formula is that he omits the second term in t^2 on the assumption that the stability of the short trajectory segments does not change or that it changes slowly compared to the other terms linear or with time. He assumes the term quadratic in t, which is connected with the stability of the short trajectory segment, to be constant.

V. MATRIX ELEMENTS BETWEEN HARMONIC OSCILLATOR EIGENSTATES

To illustrate the quality of the various approximations we have to go beyond the linear potential (since there the Airy functions are exact) and turn to excitations into harmonic potentials. Contrary to expectations based on the usual close relationship between classical and quantum dynamics in harmonic oscillators, the semiclasscial expressions for the Franck-Condon transitions are not exact and thus a useful test of our formulae.

As in the linear case, the initial state $|\Psi_i\rangle$ is a Gaussian (41) of width σ and a Gaussian Wigner transform in phase space, (55). The Hamiltonian now is

$$H = -\frac{\hbar^2}{2m}\Delta + \frac{m\omega^2}{2}q^2\,. \qquad (90)$$

The length scale $\ell = \sqrt{\hbar/m\omega}$ is characteristic of the wave length of the ground state, all higher excited states oscillate on shorter scales. It thus plays the same role as the λ

in the case of the linear potential, setting the largest scale for quantum oscillations. The Franck-Condon transitions depend on the energy and on the single parameter

$$r = \ell/\sigma = \sqrt{\frac{\hbar}{m\omega\sigma^2}}, \qquad (91)$$

which measures the size of the quantum oscillations relative to the width of the initial state.

The Wigner transform of the initial state has a maximum in phase space near $x = x_0$ and $p = 0$. The leading order classical phase space average then yields a cross section which increases up to $E_{max} \approx m\omega^2 x_0^2/2$ and decreases for higher energy. Since the quantum spectrum is discrete, the quantum transition strengths are discrete as well. A direct comparison between the leading order classical Franck-Condon spectrum

$$\rho_0(E) = \int \frac{dqdp}{2\pi\hbar} \delta(E - H(p,q))[\,,|\Psi_i\rangle\langle\Psi_i|\,]_W(p,q) \quad (92)$$

and the quantum data is shown in Fig. 5.

The quantum calculations show that for large $\hbar$ and large r the quantum cross section is shifted towards higher energies.

The Grammaticos and Voros series (25) for the harmonic oscillator can be calculated as before for the linear potential. The asymptotic expansion of the phase space trace can be carried out quite easily for the scaled Hamiltonian $H = \hbar\omega\left(\frac{1}{2}\tilde{p}^2 + \frac{1}{2}\tilde{q}^2\right)$ where $\tilde{q} = q/\ell$ and $\tilde{p} = p\ell/\hbar$. Again, there is only one operator in the series (31),

$$\mathcal{H}_2 = \frac{1}{8}\frac{\partial^2}{\partial\tilde{q}^2} + \frac{1}{8}\frac{\partial^2}{\partial\tilde{p}^2} \qquad (93)$$

and the others vanish. From the recursion relations we then find up to order $O(\hbar^8)$ with the help of MAPLE:

$$
\begin{aligned}
[\ \delta(E - \hat{H})]_W &= \delta(E - H) \\
&+ (\hbar\omega)^2 \left(-\frac{1}{8}\delta''(E - H) + \frac{1}{12}E\delta'''(E - H)\right) \\
&+ (\hbar\omega)^4 \left(\frac{5}{384}\delta^{(4)}(E - H) - \frac{3}{160}E\,\delta^{(5)}(E - H)\right. \\
&\quad \left. + \frac{160}{46080}E^2\delta^{(6)}(E - H)\right) \\
&+ (\hbar\omega)^6 \left(-\frac{61}{46080}\delta^{(6)}(E - H) + \frac{479}{161280}E\delta^{(7)}(E - H)\right. \\
&\quad \left. - \frac{11648}{10321920}E^2\delta^{(8)}(E - H) - \frac{1120}{11612160}E^3\delta^{(9)}(E - H)\right) \\
&+ (\hbar\omega)^8 \left(\frac{1385}{10321920}\delta^{(8)}(E - H) - \frac{4757}{11612160}E\delta^{(9)}(E - H)\right. \\
&\quad + \frac{1529}{6451200}E^2\delta^{(10)}(E - H) - \frac{17}{414720}E^3\delta^{(11)}(E - H) \\
&\quad \left. + \frac{1}{497664}E^4\delta^{(12)}(E - H)\right) \qquad (94)
\end{aligned}
$$

which involves derivatives of the delta function up to 12th order. Incidentally, this expansion shows rather clearly the structure of the two different series for Greek's function, one in powers of $\hbar$ (34) and one in derivatives with respect to energy, (25). Fig. 6 shows the quantum corrections for the harmonic oscillator Franck-Condon factors for different values of the expansion parameters. Two trends can be recognized: For large r, divergence sets in very early, even from the first term on, and the smaller the energy (or the smaller the local gradient of the potential) the worse the asymptotic expansion. In both cases the leading order term gives the correct qualitative shape of the Franck-Condon factor. For large energies, the higher order corrections are small and the series is close to the exact values. For lower energies, the higher order corrections increase and alternate in sign - the typical features of an asymptotic series. The oscillations increase rapidly with r so that the series becomes practically useless without re summation.

The Airy correction (69) has been computed and gives remarkable results in the extreme quantum regime: Fig. 7 shows the lowest order classical approximation to the harmonic oscillator matrix elements and the Airy function approximation. This confirms the importance of turning point corrections and tunnel trajectories in the Franck-Condon region.

VI. FINAL REMARKS

We set out to calculate quantum corrections for Franck-Condon factors in the classical phase space trace (8). In a nutshell, there are three main results: i) For the expansion based on (25) in the energy domain the situation seems to be that either the corrections are small to begin with (in which case one would be happy with the leading order result) or they are large and a resummation of the series is required as it is asymptotic at best. ii) In the time domain the expansion in the exponent, (85), provides a more useful representation and contains nonperturbative effects (the recurrence resonances). iii) The quality of the approximation in all cases is controlled by a single parameter, which may be estimated from the ratio of a de Broglie wavelength to the width of the initial state as in (46) and (91).

Clearly, the parameter controlling the convergence can be put to immediate use and can help to identify whether a classical approximation will suffice. An example will be given in the photodissociation for water [11,39].

The relationship between the series expansion in energy with its derivatives of delta functions, (25) and the exponentiated one in the time domain, (85), is subtle and at present not fully understood. The numerical observation is that it is in very good agreement with the quantum results and that no divergences seem to occur. The calculation leading to (54) for the expansion of the Airy function shows that at least in this case all divergences

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are removed instantly: the exponentiated series stops after the cubic in time. In general circumstances, this will not be the case and the series will continue. Then the question is whether the power series in time, (80), or its exponentiated version is convergent or whether at some late time, perhaps related to recurrent or periodic orbits, deviations between quantum and semiclassical time evolution become noticeable. For instance, in the case of the harmonic oscillator the propagator has an exact recurrence after half a period which can only be accounted for by a divergence of the series. The success of the present calculation in the time domain would then be related to the fact that the time evolution is followed for a short time only. However, from a practical point of view, that is all one is asking for in the calculation of the direct part in Franck-Condon transitions, and we therefore propose to use (82) with the exponentiated expansion (85) and a fast Fourier transform to the energy domain.

The formulae presented allow for an accurate semiclassical calculation of the background term and thus for the largest contribution to the cross section in predominantly direct reactions. The positions and widths of resonances can be calculated from periodic orbit expansions and zeta functions. Calculation of the cross section however again requires improved formulae which take into account the neighborhood of the trajectories and the fringes in phase space are needed. This would then allow to calculate all aspects of cross sections semiclassically. Work along those lines is in progress.

ACKNOWLEDGMENTS

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FIG. 1. Series expansion for Franck-Condon transitions onto a linear potential for a Gaussian initial state. Shown is the decadic logarithm of the relative error of the series including the first n terms taken at the energy corresponding to the center of the Gaussian.

FIG. 2. Contributions to the Wigner propagator in position space. The simplest approximation to the short time Wigner propagator uses the free one on a constant potential energy $V(\mathbf{Q})$. This is appropriate for high energies like E_1. Tunnel effects are important at lower energy E_2 and can be included by use of the propagator on the linearized potential.

FIG. 3. Contributions to the Wigner propagator in phase space. Two paths contribute to the semiclassical propagator from $Q - X/2$ to $Q - X/2$: the direct one from phase space point 2 to 3 and the path through the turning point from 1 to 3.

FIG. 4. Exact Franck-Condon factors for the transition onto a linear potential. For small s the cross section eq. (44) has a single maximum. For larger s recurrence resonances develop. In rescaled units they have a spacing given by eq. (72). In original units the oscillations become denser and denser.

FIG. 5. Comparison between the n-th harmonic oscillator eigenstate matrix elements $\langle n|\Psi_i\rangle\langle\Psi_i|n\rangle$ of the projector onto a Gaussian $\Psi_i(q)$ and the corresponding classical phase space average of the Wigner transform eq. (92). The center of the initial Gaussian remains the same for all figures. The oscillator eigenvalues are $E_n = \hbar\omega(n + 1/2)$ with $\hbar = 4.0, 2.0, 1.0, 0.25$ and $\omega = 1.0$.

FIG. 6. Quantum corrections to Frank-Condon factors for transitions to harmonic oscillator eigenstates. The different curves include all terms of eq. (94) up to the indicated order in $\hbar$. For larger energies, the corrections improve the leading order result. For low energy they develop oscillations and diverge right away.

FIG. 7. Comparison between the Weyl term, the uniform approximation and the exact results for transitions in harmonic oscillators. The exact result is shown by full circles, the Weyl term eq. (92) as a solid line and the uniform approximation eq. (69) as a dashed line.

TABLE I. Asymptotics for the cross section of a Gaussian on a linear potential: We calculate the series up to its smallest term. The number of terms included grows with decreasing expansion parameter s. $\log_{10}\triangle\rho(\varepsilon = 0)$ is the logarithm of the relative error of the series including the first n terms taken at the energy corresponding to the center of the Gaussian. For large $s > 1$ the asymptotic series is practically of no use.

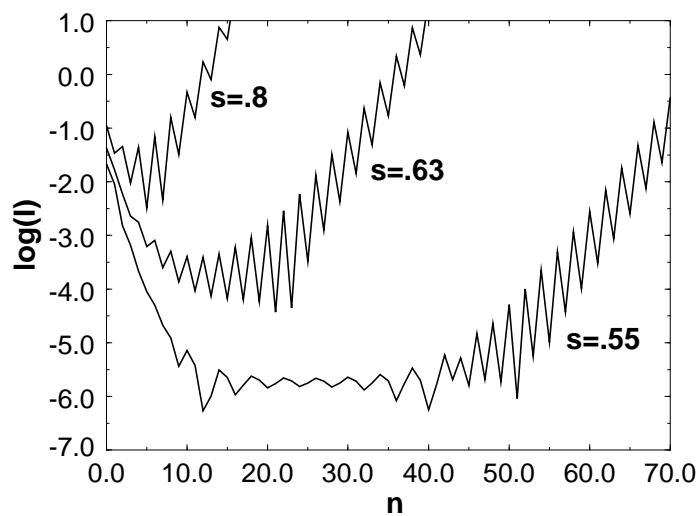| s	n	$\log_{10}\triangle\rho(\varepsilon = 0)$
1.8	0	0.03
1.6	1	-0.16
1.4	1	-0.59
1.2	1	-1.38
1.0	1	-1.68
0.8	5	-2.50
0.63	21	-4.51

Fig. 1

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Uniform semiclassical expansions for the direct part of Franck-Condon transitions
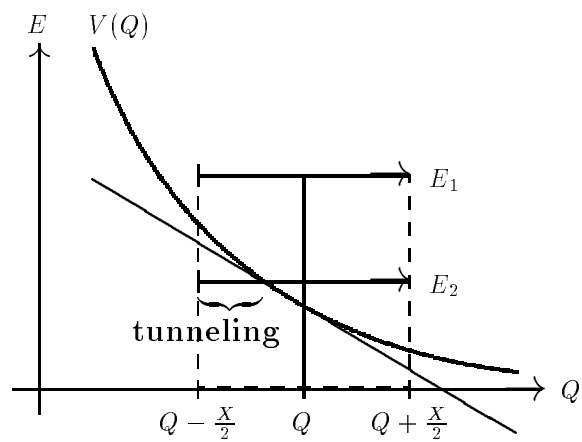
Fig. 2

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Uniform semiclassical expansions for the direct part of Franck-Condon transitions
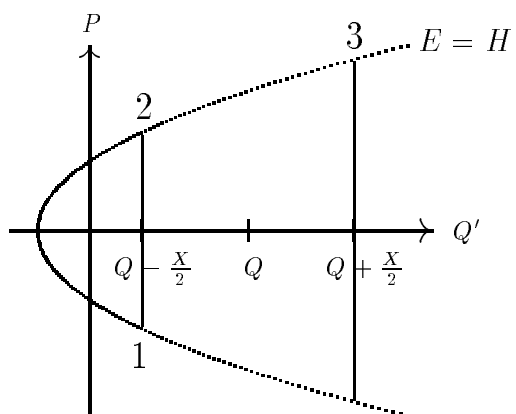
Fig. 3

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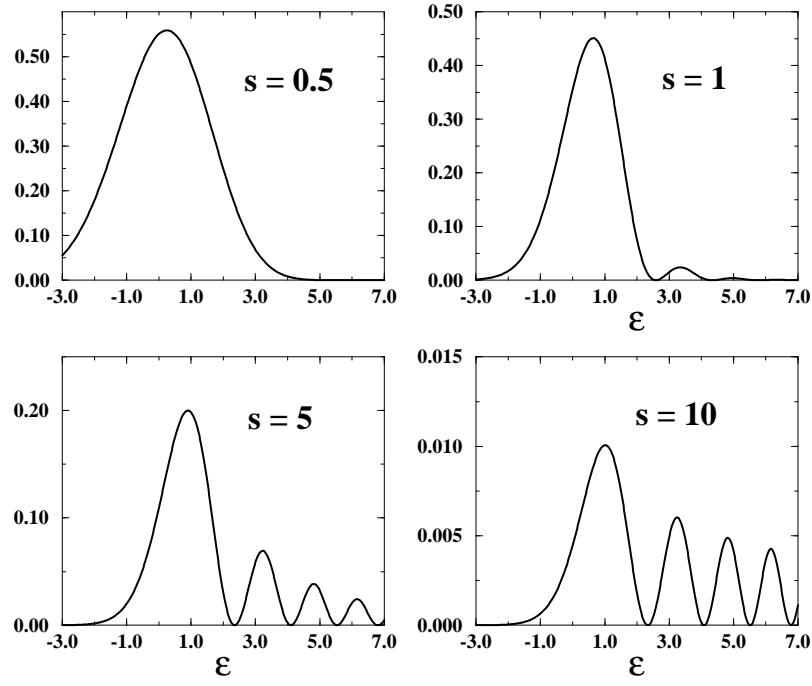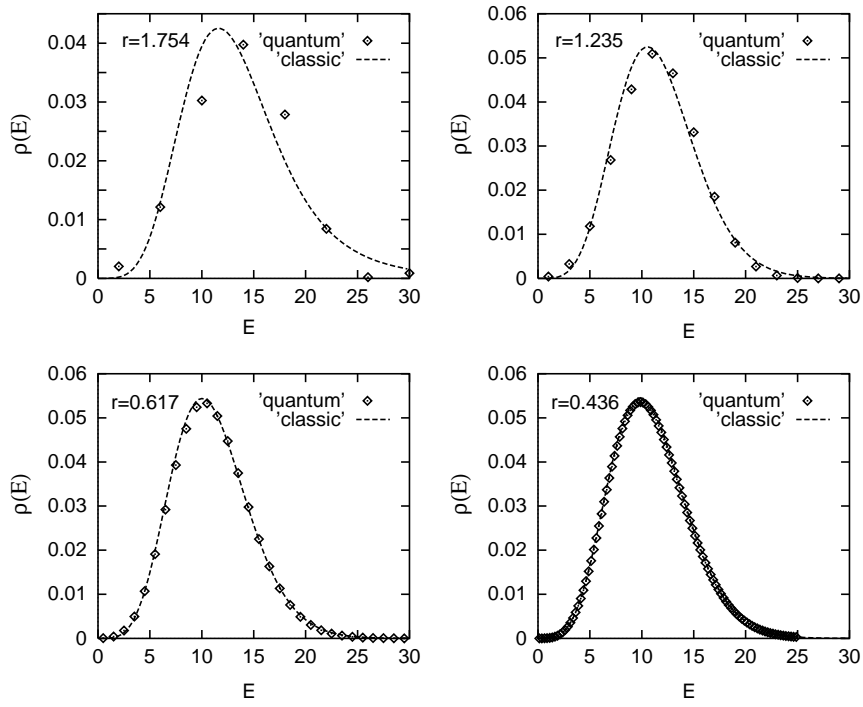Uniform semiclassical expansions for the direct part of Franck-Condon transitions

Fig. 4

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Uniform semiclassical expansions for the direct part of Franck-Condon transitions
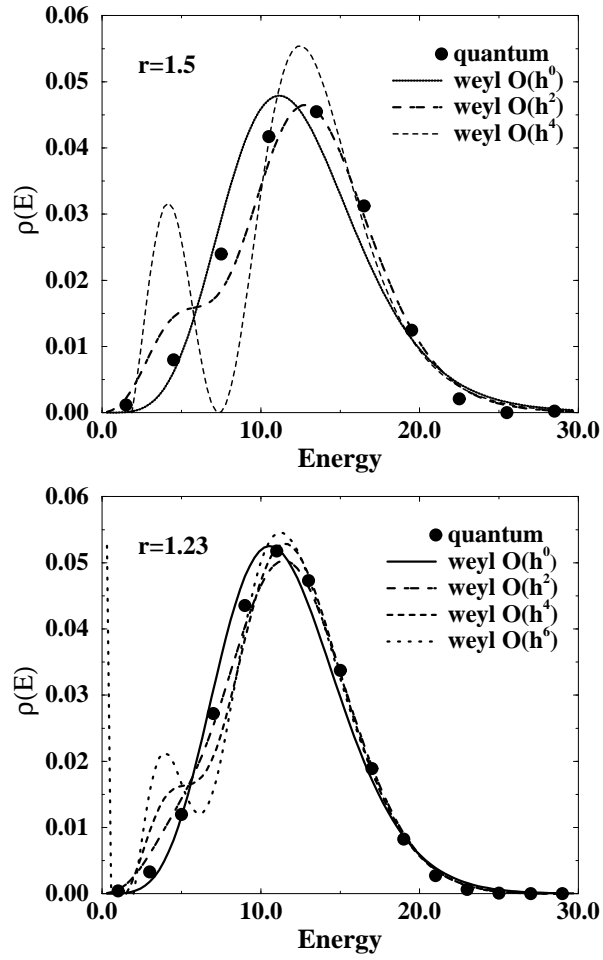
4

Fig. 5

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Uniform semiclassical expansions for the direct part of Franck-Condon transitions

Fig. 6

B. Hüpper and B. Eckhardt

Uniform semiclassical expansions for the direct part of Franck-Condon transitions
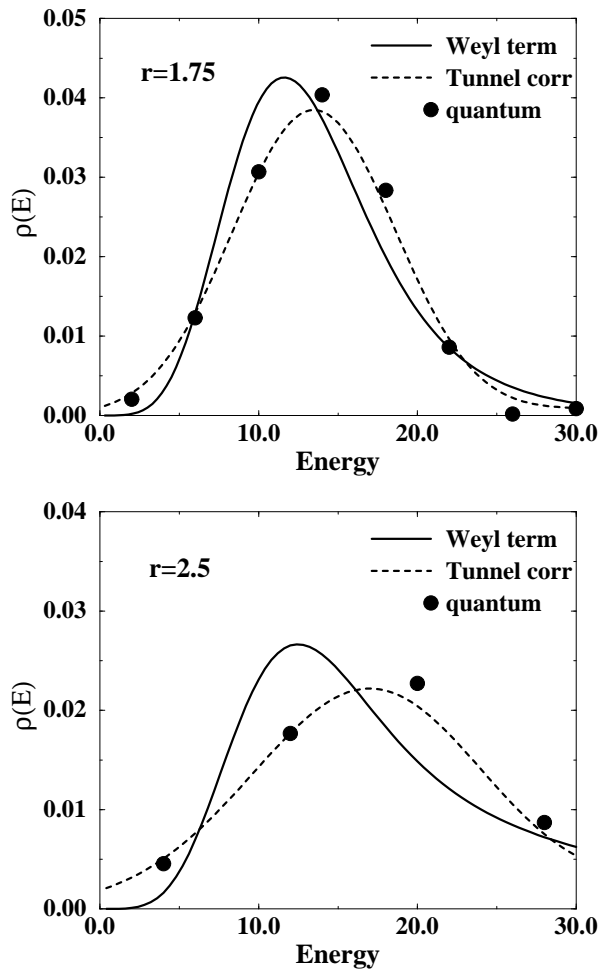
Fig. 7

B. Hüpper and B. Eckhardt

Uniform semiclassical expansions for the direct part of Franck-Condon transitions